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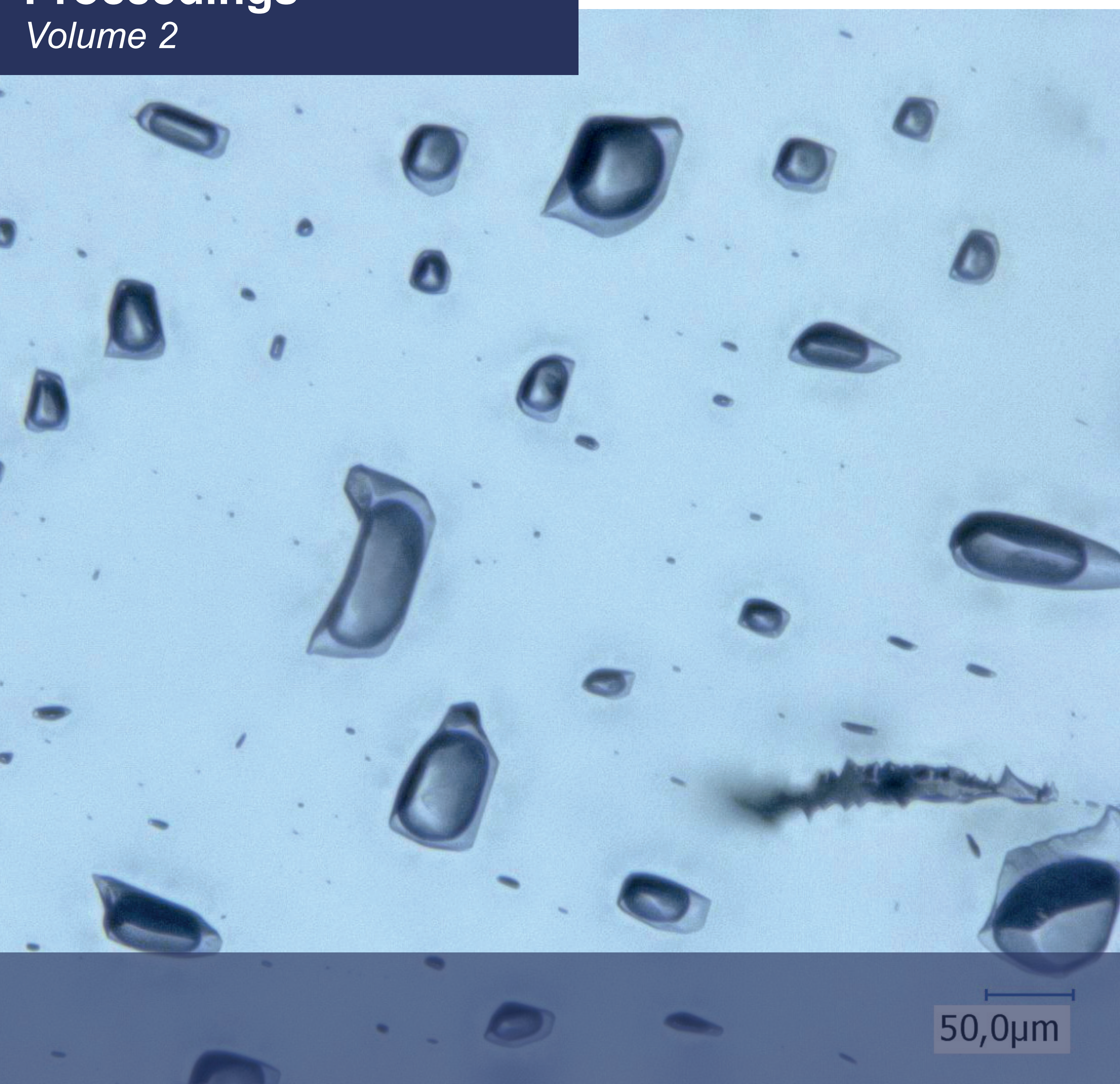
Volume 2



Mineral Resources in a Sustainable World

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Edited by
Anne-Sylvie André-Mayer, Michel Cathelineau, Philippe Muchez, Eric Pirard and Sven Sindern

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Cover photograph: CO_2-rich fluid inclusions (alpine quartz) (M. Cathelineau).

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Volume 2

Session 4 561

Developments in element and isotope geochemistry, source tracing and geochronology

Last minute cancellation

Session 5 665

Strategic metals: sources and ore-forming processes

Last minute cancellation

SESSION 4

Developments in element and isotope geochemistry, source tracing and geochronology

Convenors

Leonid Danyushevsky, Julien Mercadier, Laurie Reisberg

Rare Earth Elements Related to Major Tertiary Volcanic Complexes in the Republic of Macedonia

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Abstract. The latest REE data for analyzed samples of trachyandesite, andesite, trachydacite, dacite and rhyolite from the Sasa-Toranica, Kratovo-Zletovo and Buchim-Damjan-Borov Dol volcanic areas are presented. New REE data including negative Eu anomalies, 0.7277-0.9036, along with determined La/Yb ratios ranging from 11.9 to 29.6 confirm inferred material source from the contact zone between the lower crust and upper mantle where contamination of primary melt occured. These new data reconfirm previous results, provide slightly new insight into the Tertiary magmatism of the entire district, and suggest the exact origin of the material that produced the Tertiary magmatic rocks.

Keywords. REE, Tertiary, volcanic, Macedonia

1 Introduction

Extensive volcanic activity, accompanied by intrusion of minor plutons, took place in the Macedonian part of the Dinaride system during the Late Tertiary (Boev and Yanev 2001). These magmatic rocks represent part of a 1200 km long magmatic zone extending from southeastern Austria to Turkey (Harkovska et al. 1989). The magmatic rocks outcrop essentially in the Serbo-Macedonian massif and in the Vardar zone (Fig. 1). At the territory of the Republic of Macedonia the Tertiary magmatism prevails in its eastern parts, where the most remarkable are the Kratovo-Zletovo volcanic area, followed by the Buchim-Damjan-Borov Dol area and the easternmost Toranica-Sasa volcanic area.

The Kratovo-Zletovo is the largest magmatic area in Macedonia with a surface of 1200 km^2. It is also a very important mining area with significant Pb-Zn deposits. Volcanic rocks occurring in the area are: latites and andesites accompanied by dacites to trachydacites, andesite-dacite ignimbrites, dacite. Intrusive or plutonic rocks are represented by the quartz-monzonitic to monzonitic representatives. Many authors studied this area (Stojanov 1974; Serafimovski 1990; Stojanov and Serafimovski 1990; Serafimovski and Boev 1996).

The Buchim-Borov Dol area is a small volcanic area of high metallogenic importance because it contains the active Bucim porphyry copper deposit. According to the chemical composition, the volcanic rocks vary from latites, through trachydacites-trachytes to trachyrhyolites (Serafimovski et al. 1996; Lehmann et al. 2013).

The Sasa-Toranica area as part of the Tertiary volcanic complex in the Osogovo-Besna Kobila (Sasa-Toranica ore district) area regionally strike NW-SE for several tens of kilometers on both sides of Macedonian-Bulgrian border. Volcanic rocks are represented as dacitic tuffs, dacites, quartzlatites, rhyolites, trachy-andezites, andesite-latites and occasionally lamprophyres (Simic, 1997; Pendjerkovski 1965; Aleksandrov 1992; Serafimovski 1990, 1993; Boev and Yanev 2001).

The K-Ar absolute ages range from 31 to 14 Ma confirming Oligocene-Miocene age as previously determined by relative methods. $^{87}Sr/^{86}Sr$ ratios (0.70954 to 0.71126) suggest material is sourced from the contact zone between the lower crust and upper mantle where contamination of primary melt occured.

The aims of this paper are to summarize our latest Rare Earth Elements (REE) study and our efforts to enlighten the origin of Tertiary volcanic magmas along with some previous data for strontium isotopes.

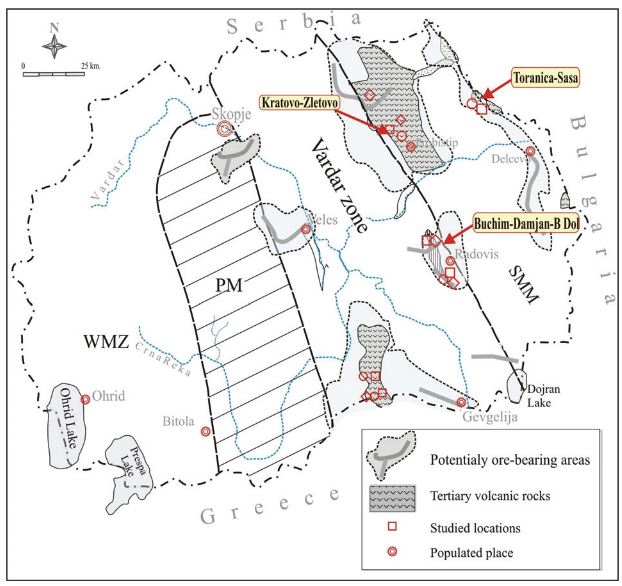

Figure 1. Simplified map of the studied areas. WMZ-Western Macedonian Zone; PM-Pelagonnian Massif; SMM-Serbo-Macedonian Massif

2 Methodology

The field sampling took place within the boundaries of earlier mentioned three Tertiary volcanic complexes, Toranica-Sasa, Kratovo-Zletovo and Buchim-Damjan-Borov Dol. Twelve rock samples were sampled, four for each complex. After detailed sampling and preparation (rock samples were sieved and finely powdered) at the Faculty of Natural and Technical Sciences, University "Goce Delcev" in Stip, Republic of Macedonia, samples were sent to the Actlabs in Canada (INAA REE analysis). Achieved analytical precision was better than 5%.

3 Results and discussion

As we already mentioned, selection of twelve samples from Tertiary magmatic rocks from Eastern Macedonia were analyzed for REE concentrations. REE concentration data for twelve samples are presented in Table 1 and plotted in a chondrite-normalized spider diagram (Figure 2).

Table 1. Rare earth elements in rocks from the Toranica-Sasa, Kratovo-Zletovo and Buchim-Damjan-Borov Dol (in ppm).

Sample / Element	TS1	TS7	TS9	TS13	KZ2	KZ5	KZ7	KZ8	BD1	BD4	BD5	BD6
La	53.10	52.01	39.64	44.88	58.40	32.65	50.66	28.64	32.78	68.27	44.86	67.52
Ce	106.42	95.41	72.06	79.32	106.24	61.09	90.39	53.91	59.54	119.26	86.72	118.34
Pr	13.35	11.36	8.08	9.72	12.07	7.35	9.98	6.25	7.12	13.64	10.47	12.99
Nd	52.49	42.14	28.26	35.24	43.59	27.53	35.17	22.76	27.07	48.20	38.80	45.95
Sm	9.25	7.48	5.07	6.79	7.72	5.42	5.92	4.30	5.14	8.32	7.00	7.66
Eu	2.22	1.68	1.11	1.65	1.79	1.40	1.34	1.13	1.45	2.00	1.52	1.86
Gd	7.27	5.86	4.28	6.48	6.12	5.03	4.95	4.09	4.70	6.79	5.56	6.14
Tb	0.93	0.78	0.61	0.98	0.80	0.80	0.70	0.65	0.71	0.88	0.75	0.80
Dy	4.47	3.98	3.30	5.24	4.18	4.53	3.71	3.77	3.87	4.51	3.78	4.30
Ho	0.78	0.73	0.64	1.00	0.78	0.93	0.71	0.74	0.78	0.83	0.69	0.80
Er	2.15	2.09	1.82	2.75	2.20	2.68	2.09	2.20	2.25	2.33	1.91	2.34
Tm	0.30	0.31	0.28	0.38	0.33	0.42	0.33	0.34	0.34	0.33	0.28	0.33
Yb	1.98	2.02	1.87	2.30	2.14	2.74	2.13	2.21	2.26	2.30	1.89	2.31
Lu	0.30	0.30	0.29	0.35	0.32	0.41	0.31	0.35	0.33	0.34	0.28	0.34

TS1-Trachydacite; TS7-Trachydacite; TS9-Dacite; TS13-Dacite; KZ-2Trachydacite; KZ-5 Trachyandesite; KZ-7 Rhyolite; KZ-8 Dacite; BD-1 Trachyandesite; BD-4 Trachyandesite; BD-5 Trachydacite; BD-6 Trachydacite.

According to data of rare earth elements concentrations in Table 1, chondrite-normalized REE plot according to Sun and McDonough (1989) is displayed in Figure 2 below, to show the REE concentration pattern in the Tertiary magmatic rocks in the areas of interest.

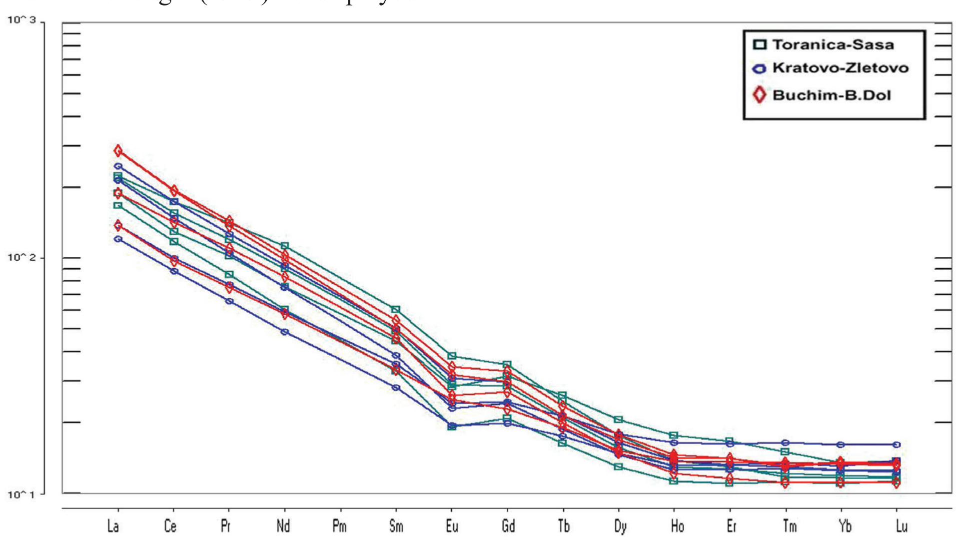

Figure 2. REE plot of chondrite normalized values (Sun and McDonough, 1989) in samples from the Tertiary magmatic rocks in the areas of interest

From the plot above is observed that there is a relative enrichment of Light Rare Earth Elements (LREE, La-Nd) over Heavy Rare Earth Elements (HREE, Er-Lu) (Figure. 2) in the Tertiary magmatic rocks from the Eastern Macedonia. This could be due to fractionation of LREE and their increase compared to chondrite values (Rollinson 1992). Such a fractionation the most often is consequence of partial melting that according to the curve slope is not of some higher intensity.

Another parameter used to describe REE data is the europium anomaly (Eu/Eu*), which is based on an idealized, smooth REE distribution. Europium, like the other lanthanides, occurs in a trivalent ($^{3+}$) oxidation state, but can also be reduced to ($^{2+}$) under certain conditions. Europium anomalies are primarily due to the preferential incorporation of the divalent form into plagioclase as a substitute for strontium ($^{2+}$) in reducing magmas (Taylor and McLennan 1981, 1995). Observing the middle part of our plots we found that there are slight deviations of Eu, from the supposed "ideal" line between the Sm and Gd. In that direction were calculated Eu anomalies, as a geometric mean, by the equation (Taylor and McLennan 1981, 1985, 1995; Fu et al. 2010a, 2010b):

$$Eu / Eu^{*} = \frac{Eu_N}{\sqrt{[(Sm_N) \cdot (Gd_N)]}}$$

where: Eu/Eu* - represents the ratio of the actual concentration of europium in the sample to the ideal concentration, assuming an REE distribution profile matching that of a reference material, in this case chondrites (dimensionless),

$[Eu]_N$ - the chondrite-normalized concentration of europium (dimensionless),

$[Sm]_N$ - the chondrite-normalized concentration of samarium (dimensionless), and

$[Gd]_N$ is the chondrite-normalized concentration of gadolinium (dimensionless).

Values of Eu/Eu* greater than 1.0 indicates a positive anomaly while a value less than 1.0 is considered negative anomaly (Taylor and McLennan 1985). In such manner calculated values are displayed within the Table 2:

Table 2. Eu anomaly values calculated for particular samples of Tertiary rocks.

Sample	Eu anomaly value
TS1	0.8289057
TS7	0.7740283
TS9	0.7276697
TS13	0.7597480
KZ2	0.7976541
KZ5	0.8224152
KZ7	0.7556627
KZ8	0.8205586
BD1	0.9036076
BD4	0.8133085
BD5	0.7441942
BD6	0.8274635

Calculated values of Eu/Eu^* anomalies confirmed slightly negative Eu anomaly, ranging from 0.7276697 to 0.9036076 for the entire set of samples (coupled with the mean Eu/Eu^* value of 0.7979347) or by areas, Toranica-Sasa (0.7276697-0.8289057), Kratovo-Zletovo (0.7556627-0.8224152) and Buchim-Borov Dol (0.7441942-0.9036076). These values suggest that the plagioclase was separated from the magma prior to solidification and the rock formed resulted with depletion of europium (Taylor and McLennan 1981, 1985; Rollinson 1992), due to processes of fraction crystalization or partial melting of rock(s) that contained feldspar, which was indicated by the variations of Ba and Sr contents relative to Rb and variation of Y, too. As it is known the fractionation in these areas, judging by the slope of plot curve is of medium to small intensity, which is in direct line with studies of porphyry Cu-Mo and some other polymetallic deposits around the World that are related with ocean and continental arc settings of Cenozoic age (Titley and Beane 1981; Richards 2003; Cooke et al. 2005), while only rarely are being related to old folded belts where both sides are characterized by compression tectonic setting and thinned continental crust (Titley and Beane 1981).

The degree of REE fractionation, can be expressed as concentration ratio of light REE (La or Ce) versus concentration of heavy REE (Yb or Y). Ratio $(La/Yb)_N$ often is plot versus Ce_N or Yb_N at two variables plot and represents measure of degree of REE fractionation. In our study we prepared plots displaying REE fractionation versus concentration change of REE at Figure 3a (La/Yb vs. Yb) and Figure 3b (La/Yb vs. Yb)

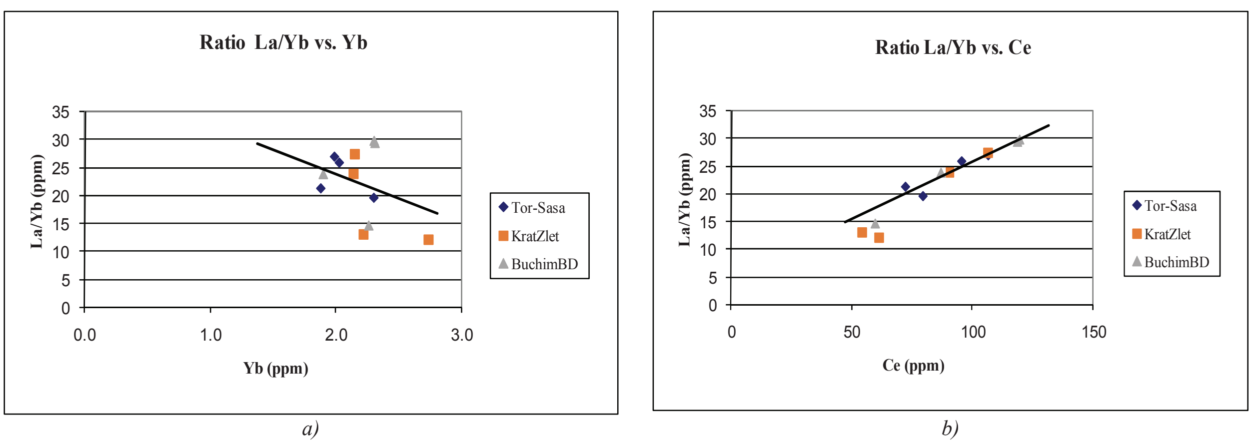

Figure 3. Degree of REE fractionation versus REE concentration change in samples from Toranica-Sasa, Kratovo-Zletovo and Buchim-Borov Dol areas. The relation is bivariate and displayed as ratio: a) between La/Yb vs. Yb and b) La/Yb vs. Ce (values were normalized to chondritic ones).

From the plot on Figure 3*a*, can be seen that with the increase of HREE (Yb) fractionation of REE decreases, while from the plot on Figure 3b, au contrary to the previous one (Figure 3a), it can be seen that with the increase of LREE the fractionation increases.

5 Conclusion

In general REE data from samples taken from the Toranica-Sasa, Kratovo-Zletovo and Buchim-Damjan-Borov Dol volcanic areas, confirmed that there is a relative enrichment of LREE over HREE in the Tertiary magmatic rocks from the Eastern Macedonia probably due to supposed fractionation of LREE and their increase compared to chondrite values, which could be attributed to partial melting that was not of some higher intensity. Calculated values of Eu/Eu^* anomalies confirmed slightly negative Eu anomaly (0.7276697 - 0.9036076) for the entire set of samples (mean value of 0.7979347), which suggests that plagioclase was separated from the magma prior to solidification and the rock formed resulted with depletion of europium due to processes of fraction crystalization or partial melting of rock(s) that contained feldspar. Ratio $(La/Yb)_N$ compared to Ce_N or Yb_N values, as a represent of degree of REE fractionation indicated to us that with the increase of HREE (Yb) fractionation of REE decreases, while au contrary, with increase of LREE (Ce) fractionation increases.

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